CANADA
DEPARTMENT OF ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

PHYSICAL METALLURGY DIVISION
INTERNAL REPORT PM-R-74-4

EFFECT OF COPPER ADDITIONS ON SINTERABILITY OF HYPEREUTECTIC Al-Si POWDER METALLURGY ALLOYS

by

C. F. Dixon and H. M. Skelly
Nuclear and Powder Metallurgy Section

May 13, 1974

90-04661/

PHYSICAL METALLURGY DIVISION
INTERNAL REPORT PM-R-74-4

EFFECT OF COPPER ADDITIONS ON SINTERABILITY OF HYPEREUTECTIC Al-Si POWDER METALLURGY ALLOYS

by

C. F. Dixon* and H. M. Skelly**

- - - - - - - -

ABSTRACT

Blending of hypereutectic Al-Si pre-alloyed powder with additions of copper and aluminum powders was investigated for possible improvement in the sinterability of the basic material after cold pressing. Although some improvement was found by adding from 1-5% Cu to Al-35% Si, the tensile strength was low in comparison to that for the same basic powder metallurgy material fabricated by hot pressing. The method of powder blending was found to have no significant effect.

---

*Physical Scientist and **Research Scientist, Nuclear and Powder Metallurgy Section, Physical Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

INTRODUCTION

Hypereutectic Al-Si powder metallurgy (P/M) alloys containing a fine dispersion of up to 45%Si have been developed in these laboratories[1,2]. Consolidation of the alloys is accomplished by hot pressing or extruding, but production would be simplified and more attractive economically if they could be sintered.

Sintering of aluminum P/M alloys is seriously hindered because the powder particles are enveloped in a refractory oxide film that is not reduced by ordinary sintering atmospheres. Cremer and Cordiano[3] in 1943, sintered pure aluminum powder and also pure aluminum powder blended with copper, magnesium, and manganese powders. They thought that high compacting pressures deformed the soft aluminum particles and dislodged the oxide film sufficiently to cause clean interparticle contact. Despite this work and that of a number of other investigators[4-9], sintering of aluminum powders has only recently become a commercial proposition. Dudas and Dean[10] blended copper and magnesium powders with air atomized low-alloy aluminum powder and sintered at a temperature sufficiently high to cause localized fusion of low-melting eutectics. This promoted diffusion of the alloying additions (Cu and Mg) and resulted in high sintered strength.

The purpose of the present work was to determine if a similar technique could be used to improve the sinterability of hypereutectic Al-Si powders. The effect of 1 to 5% copper powder and 12% aluminum powder additions (by blending) on the sinterability of Al-35% Si and Al-40% Si pre-alloyed atomized powders was examined.

Two methods of mixing the powders were also examined - blending in a twin-shell blender or a Waring Blendor and grinding in an attritor. Blending is mainly a mixing action with little or no change in the shape or size of the powder particles. Grinding in the attritor, on the other hand, is a severe mechanical action. It was thought that grinding would break up the oxide film on the Al-Si alloy particles and smear them with aluminum and copper, so creating a favourable condition for diffusion to occur during sintering.

To assess the degree of sintering, the tensile strength, density and electrical resistivity of sintered specimens were determined. Tensile strength is a well-known method of determining the degree of sintering.

While it is generally accepted that density is related to tensile strength, the relationship is neither direct nor reliable since, in some cases, the density of sintered metal powder compacts decreases on sintering. Electrical resistivity, which is a rapid, non-destructive, and simple method of determining sinterability, has been shown by other investigators[11-16] to be closely related to tensile strength, but more sensitive to changes occurring during the early stages of sintering. The relationship between electrical resistivity and tensile strength as well as density for hypereutectic Al-Si alloys was examined.

EXPERIMENTAL PROCEDURE

Preparation of Powders

Pre-alloyed Al-35% Si and Al-40% Si powders were prepared by alloying aluminum (99.99% purity), silicon (99.1% purity), and an Al-48.5% Si hardener (0.26% Fe) in a silicon carbide crucible coated with china clay and heated in a resistance furnace. Melts of about 2 kg were treated with a chlorinated hydrocarbon degassing tablet, skimmed, and poured into an apparatus in which jets of compressed air atomized a stream of molten metal into powder that was quenched in water. In addition to the pre-alloyed powders, pure aluminum powder was also atomized. The powders were air dried and sieved. The minus 149 μm (100-mesh) fractions were retained for further processing.

Mixing of Powder

To prepare the powder blends shown in Table 1, minus 149 μm (100-mesh) Al-35% Si and Al-40% Si powders were mixed with electrolytic copper powder (90% minus 44 μm, 325-mesh) and with minus 149 μm (100-mesh) pure aluminum powder. The blends containing 1 and 3% copper powder were mixed for 15 min in a twin-shell blender and the Al-35% Si + 5% Cu as well as the Al-40% Si + 12% Al + 5% Cu blends were mixed for 5 min in a Waring Blendor. Some of the latter blend was also ground under alcohol in an attritor for 1/2 hr.

Pressing and Sintering Powders

Specimens for electrical resistivity measurements, 7.3 cm long by 1.3 cm in dia, were isostatically cold pressed at 344.7 MN/m^2. However, specimens made from Al-40% Si + 12% Al + 5% Cu powder that was ground in the

TABLE 1

Alloy Composition (wt %)

Nominal Composition	Chemical Analysis		
	Si	Cu	Fe
Al-35% Si	35.07		ND
Al-35% Si + 1% Cu	34.90	1.48	0.08
Al-35% Si + 3% Cu	34.24	2.93	0.11
Al-35% Si + 5% Cu	33.66	4.70	0.10
Al-40% Si + 12% Si + 5% Cu	33.80	4.34	0.14
Al-40% Si	39.68	-	ND

ND - not determined

attritor broke on handling, and to obtain strong specimens of this blend it was necessary to reduce the pressure to 172.4 MN/m^2.

Tensile specimens, 8.9 cm long and about 0.6 cm square at the gauge section, were moulded-to-shape in a double-action die according to Metal Powder Industries Federation (MPIF) Standard 10-63. Pressing was done in a 89 MN hydraulic press at 344.7 MN/m^2.

No lubricant was mixed with the powders but, during compacting with the hydraulic press, stearic acid was applied to the walls of the compacting die.

Sintering was done in vacuum (<0.2 pascals) in a tube furnace at 565, 585, and 595°C (1050, 1085, and 1100°F) for times of 1/4, 1/2, 2, 4, and 6 hr. Specimens were cooled in the furnace.

Testing of Sintered Specimens

Electrical resistivity was determined by placing probes at each end of cylindrical specimens. A current flowed through the specimen and the difference in voltage, ΔV, between two points along the length of the specimen was measured (see Figure 1). Resistivity was calculated according to the equation developed by Gegenwarth[17].

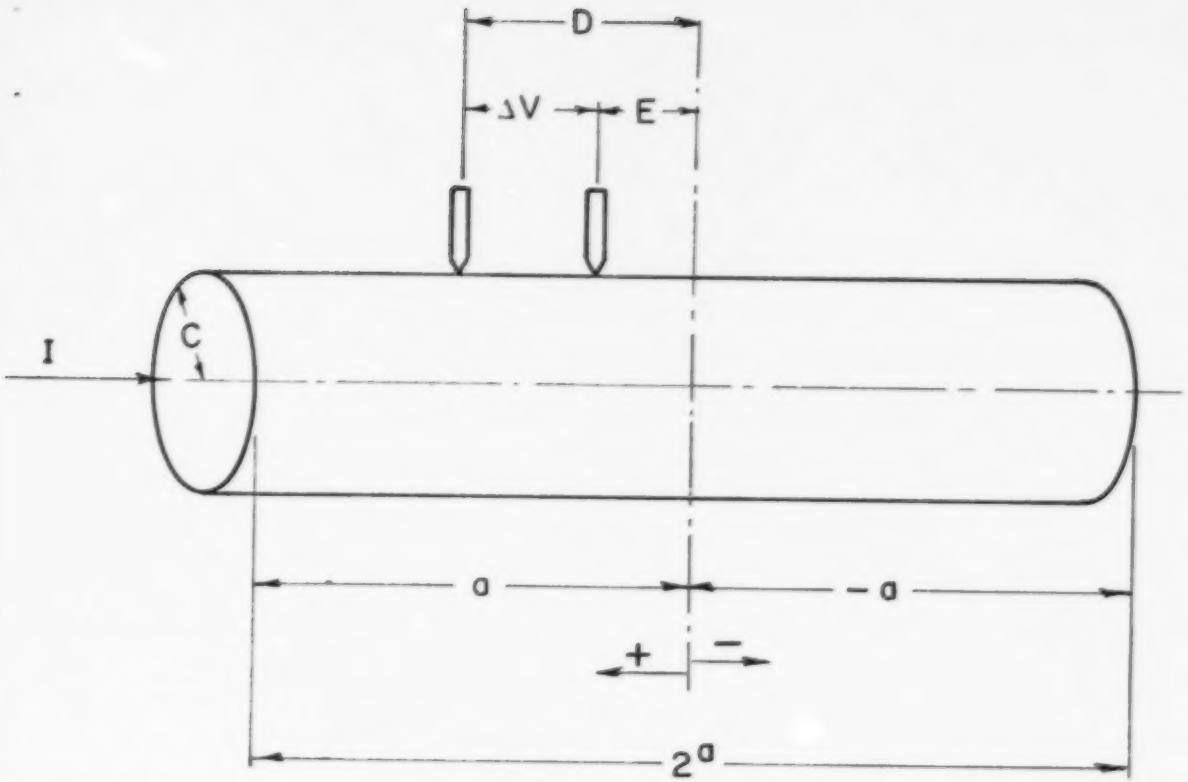


Figure 1. Conducting Cylinder

$$\rho = \frac{\pi^2 C}{4F} \cdot \frac{\Delta V}{I}$$

where

ρ = resistivity (μ ohm-cm)

C = radius of specimen (cm)

I = current through specimen (amps)

$$F = \sum_1^{\infty} \sin \frac{\eta\pi}{2} \cos \frac{\eta\pi (D+E)}{4a} \cdot \sin \frac{\eta\pi(D-E)}{4a} \cdot \frac{1}{\eta I\left(\frac{\eta\pi C}{2a}\right)}$$

D-E = distance between probes (cm)

D+E = 0 when points equally spaced about the mid-length of the specimen

2a = length of specimen (cm)

To check the accuracy of this method of determining resistivity, measurements were made on a cylinder of pure aluminum. The experimental value was 2.7 μ ohm-cm as compared to a published value of 2.8 μ ohm-cm[18].

Tensile tests were done on an Instron machine.

Densities were determined on sintered specimens after tensile testing. A section of the specimen was coated with lacquer and then weighed in air and water according to MPIF Standard 8-50.

Metallographic Examination and Chemical Analysis

For microexamination, samples of the minus 149 μm (100-mesh) Al-35% Si and Al-40% Si powders were mixed with plastic epoxide to make a slurry which was poured into bakelite mounting rings and allowed to set at room temperature. After setting, these specimens were ground on silicon carbide paper to a 600 grit and then polished on Microcloth with Linde A and Linde B. Cross sections of all tensile specimens also were mounted in plastic epoxide and polished as above.

The chemical analyses in Table 1 were done on samples of the powders.

RESULTS AND DISCUSSION

Properties of Powders

Figure 2 is a photomicrograph of the Al-35% Si powder showing a fine distribution of primary silicon particles in each grain. The structure of the Al-40% Si powder is similar except for the presence of more primary silicon particles.

Chemical analyses of the powders and powder blends given in Table 1 show the silicon content of the Al-35% Si powder to be 35.01%. This percentage is appropriately reduced when the powder is blended with 1, 3, and 5% copper powder. Table 1 also shows the nominal Al-40% Si powder to contain 39.68% Si, which is reduced to 33.80% when this powder is blended with 12% aluminum and 5% copper powders. The copper contents of the blends were considered satisfactory for this investigation. The iron in the powders originates in the Al-Si hardener used to make the pre-alloyed powders.

The sieve analyses for the powders used to make the blends and also for the Al-40% Si + 12% Al + 5% Cu blend after grinding in the attritor for 1/2 hr are listed in Table 2. The large minus 44 μm (325-mesh) fraction (51.5%) in the blend ground in the attritor was due to both the grinding action and to the addition of the fine copper powder (90% minus 44 μm, 325 mesh). This large amount of fines could be the reason for the problem, previously mentioned, in obtaining strong green compacts.

TABLE 2

U. S. Standard Sieve Analyses

Powder	% −149μm+105μm (−100+140)	% −105 μm+74μm (−140+200)	% −74μm+63μm (−200+230)	% −63μm+44μm (−230+325)	% −44μm (−325)
Al	30.7	27.3	12.2	13.5	16.3
Al-35% Si	40.7	22.0	12.5	11.8	12.5
Al-40% Si	28.2	20.5	14.5	15.2	21.7
Al-40% Si + 12% Al + 5% Cu*	11.5	6.5	9.6	19.9	51.5
Cu %	0.4	1.6	0.90	7.0	90.0

*Ground in attritor

Figure 2. Al-35% Si Minus 149 μm (100-mesh) Powder. X150.

Properties of Sintered Powders

Electrical Resistivity

The electrical resistivities for Al-35% Si and Al-35% Si + 1 to 5% Cu sintered specimens are listed in Table 3. Data for hot-pressed Al-35% Si material are also included for comparison purposes. These results show the resistivity to vary between 49.3 μ ohm-cm for an Al-35% Si specimen sintered at 565°C (1050°F) for 1/2 hr, to 11.8 μ ohm-cm for an Al-35% Si + 1% Cu specimen sintered at 585°C (1085°F) for 6 hr. These values can be compared to a resistivity of 8.9 μ ohm-cm for the Al-35% Si hot-pressed material.

Plots of resistivity versus sintering time for specimens containing 0 to 5% Cu in Figure 3 show that blending with copper powder decreases the resistivity. This would indicate improvement in the sinterability of Al-35% Si specimens sintered at 565°C (1050°F) assuming that the reduction in resistivity is a result of increased sinterability and not of an increase in conductivity resulting from the presence of copper as a good conducting medium. Tensile results, discussed later, show that the added copper does in fact increase the sinterability of the sintered specimens as is indicated by the resistivity measurements.

Increasing the sintering temperature to 585°C (1085°F) reduces the resistivity of all specimens, but, in these specimens the effect of copper on resistivity is much less. Increasing the sintering time also decreases the

TABLE 3

Properties of Sintered Powders

Powder	Sintering		Resistivity	UTS	Density
	Temp (°C)	Time (hr)	(μ ohm-cm)	(MN/m^2)	(g/cc)
Al-35% Si	565	1/2	49.3	4.2	1.96
Al-35% Si	565	2	38.6	4.1	1.96
Al-35% Si	565	4	28.0	8.5	1.94
Al-35% Si	585	1/2	25.5	4.6	1.95
Al-35% Si	585	4	13.7	30.0	2.06
Al-35% Si + 1% Cu	565	1/2	35.9	8.5	1.94
Al-35% Si + 1% Cu	565	2	17.7	14.3	1.94
Al-35% Si + 1% Cu	565	4	16.6	17.9	1.95
Al-35% Si + 1% Cu	585	1/2	25.2	-	-
Al-35% Si + 1% Cu	585	2	23.6	-	-
Al-35% Si + 1% Cu	585	4	12.6	-	-
Al-35% Si + 1% Cu	585	6	11.8	-	-
Al-35% Si + 3% Cu	565	1/2	26.6	7.6	1.93
Al-35% Si + 3% Cu	565	2	18.0	13.2	1.93
Al-35% Si + 3% Cu	565	4	16.9	-	-
Al-35% Si + 3% Cu	565	6	14.4	-	-
Al-35% Si + 3% Cu	585	1/2	23.6	-	-
Al-35% Si + 3% Cu	585	6	12.0	45.3	2.19
Al-35% Si + 5% Cu	565	1/2	30.7	-	-
Al-35% Si + 5% Cu	565	4	15.0	-	-
Al-35% Si + 5% Cu	585	1/2	23.8	-	-
Al-35% Si + 5% Cu	585	4	13.1	43.9	2.15
Al-40% Si+12% Al+5% Cu*	565	1/2	55.8	-	-
Al-40% Si+12% Al+5% Cu	565	4	16.9	-	-
Al-40% Si+12% Al+5% Cu*	585	1/2	34.8	-	-
Al-40% Si+12% Al+5% Cu*	585	4	16.0	-	-
Al-40% Si+12% Al+5% Cu*	595	1/4	45.8	-	-
Al-40% Si+12% Al+5% Cu*	595	1/2	31.8	-	-
Al-40% Si+12% Al+5% Cu	595	1/4	39.6	-	-
Al-40% Si+12% Al+5% Cu	595	1/2	31.1	-	-
Al-35% Si (Hot Pressed)	-	-	8.9	173.0	2.50

*Ground in attritor.

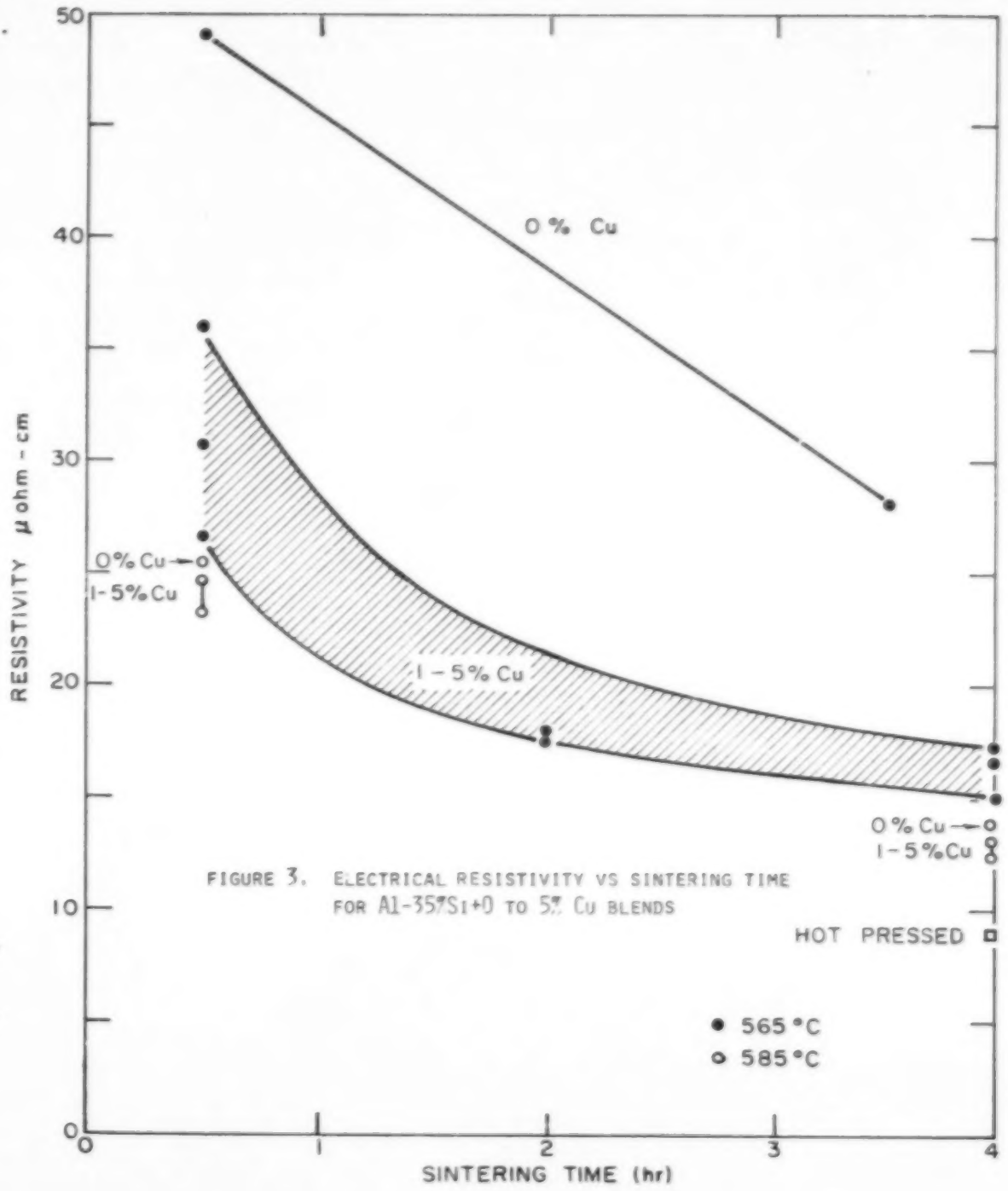


FIGURE 3. ELECTRICAL RESISTIVITY VS SINTERING TIME FOR Al-35%Si+0 TO 5% Cu BLENDS

resistivity at both temperatures.

From plots in Figure 4 of resistivity versus per cent copper for different sintering times, it appears that, for specimens sintered at 565°C (1050°F) for 1/2 hr, maximum reduction in resistivity is obtained with 3% Cu. For specimens sintered for 2 and 4 hr, the maximum reduction in resistivity occurs at 1% Cu. Figure 4 also shows that, for equal sintering times, copper additions to specimens sintered at 565°C (1050°F) are not as effective as increasing the sintering temperature to 585°C (1085°F). It should be noted that sweating occurred in some specimens, but was most pronounced for sintering at 585°C (1085°F) for times longer than 1/2 hr.

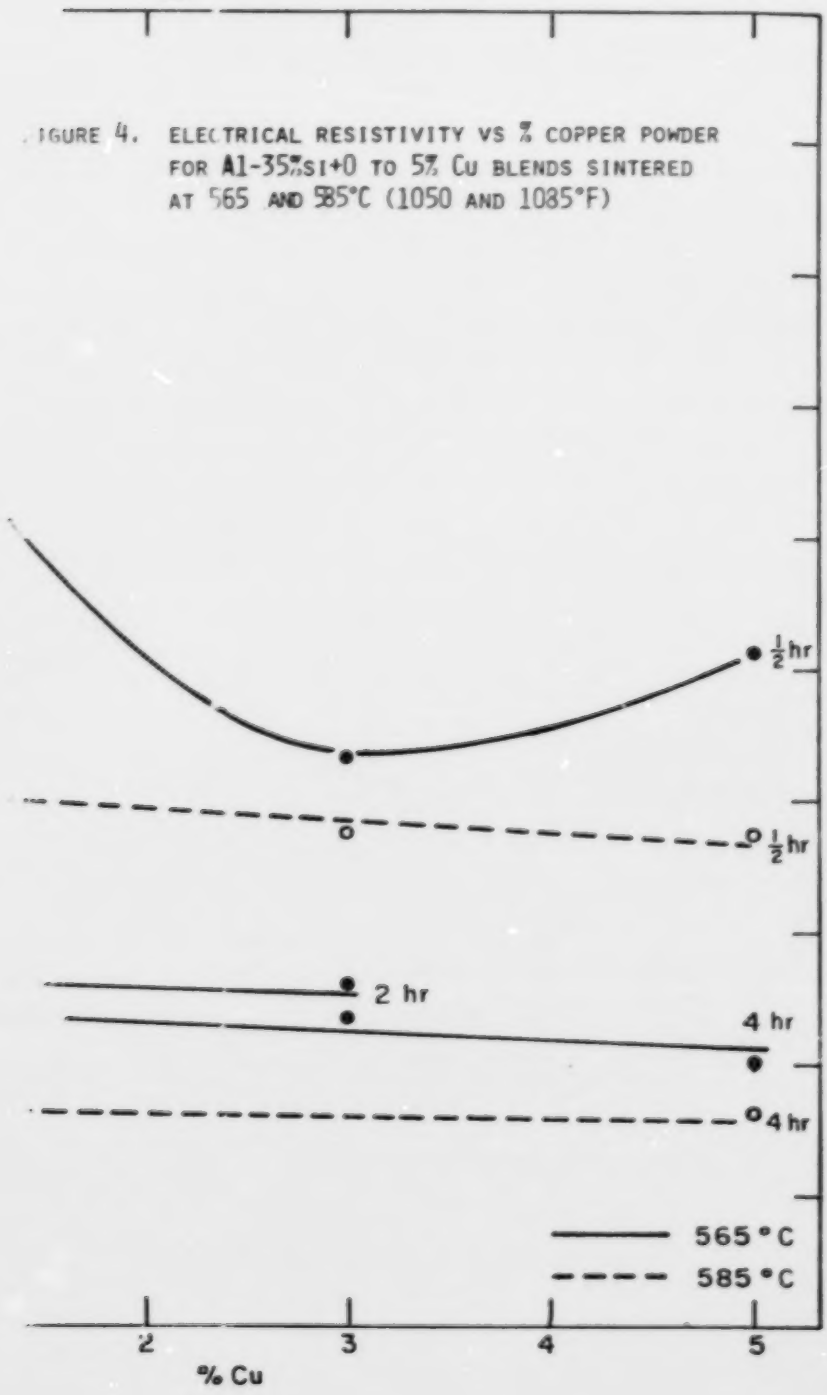
Resistivities for the sintered specimens of the Al-40% Si + 1.5% Al + 5% Cu mixtures that were prepared in a Waring Blendor or ground in an attritor are included in Table 3. These results show that grinding of the powders did not improve the sinterability. The results also show that sintering at 595°C (1100°F) for 1/4 and 1/2 hr did not result in any significant improvement.

Tensile Strength

To determine the relationship between electrical resistivity and tensile strength, a number of specimens with resistivities varying from 12 to 49.3 μ ohm-cm were selected for testing. Results are listed in Table 3 and plotted against resistivity values in Figure 5. The plot shows that for resistivities above 20 μ ohm-cm and tensile strengths below 10 MN/m^2 there is a noticeable change in resistivity with no apparent change in tensile strength. This shows, as was expected, that the resistivity is more sensitive to changes in the structure of the specimens during the early stages of sintering. At the other end of the plot the tensile strength is more sensitive.

The effect of copper additions on improving the sinterability of Al-35% Si specimens sintered at 565°C (1050°F), indicated by the resistivity measurements, is also reflected in the tensile strengths. This can be seen by examining the plots of tensile strength versus sintering time for Al-35% Si and Al-35% Si + 1% Cu sintered specimens in Figure 6. These results show that the decrease in resistivity (Figures 3 and 4) was a result of increased sinterability and not of the presence of copper as a conductor.

FIGURE 4. ELECTRICAL RESISTIVITY VS % COPPER POWDER FOR Al-35%Si+0 TO 5% Cu BLENDS SINTERED AT 565 AND 585°C (1050 AND 1085°F)



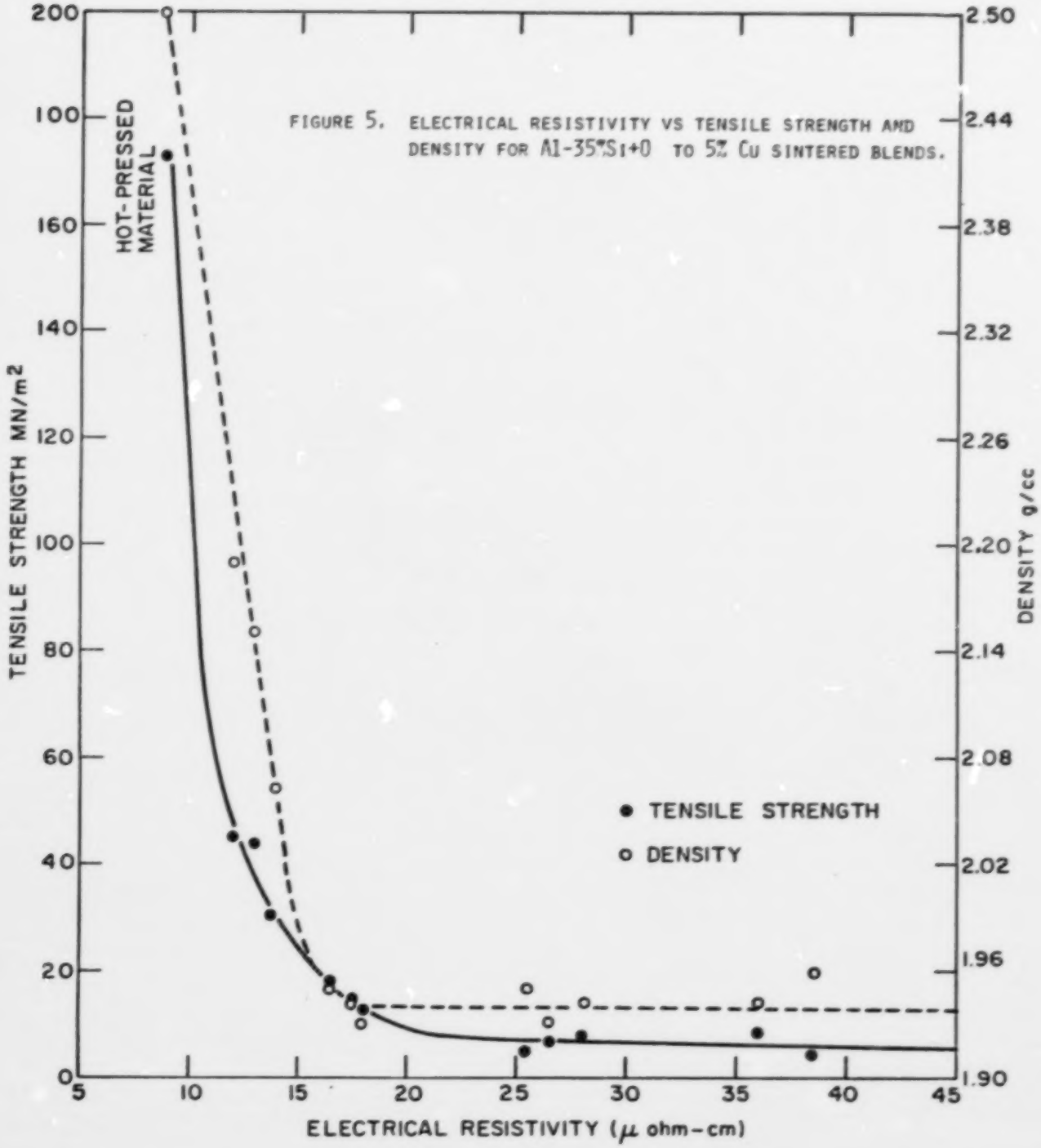


FIGURE 5. ELECTRICAL RESISTIVITY VS TENSILE STRENGTH AND DENSITY FOR Al-35%Si+0 TO 5% Cu SINTERED BLENDS.

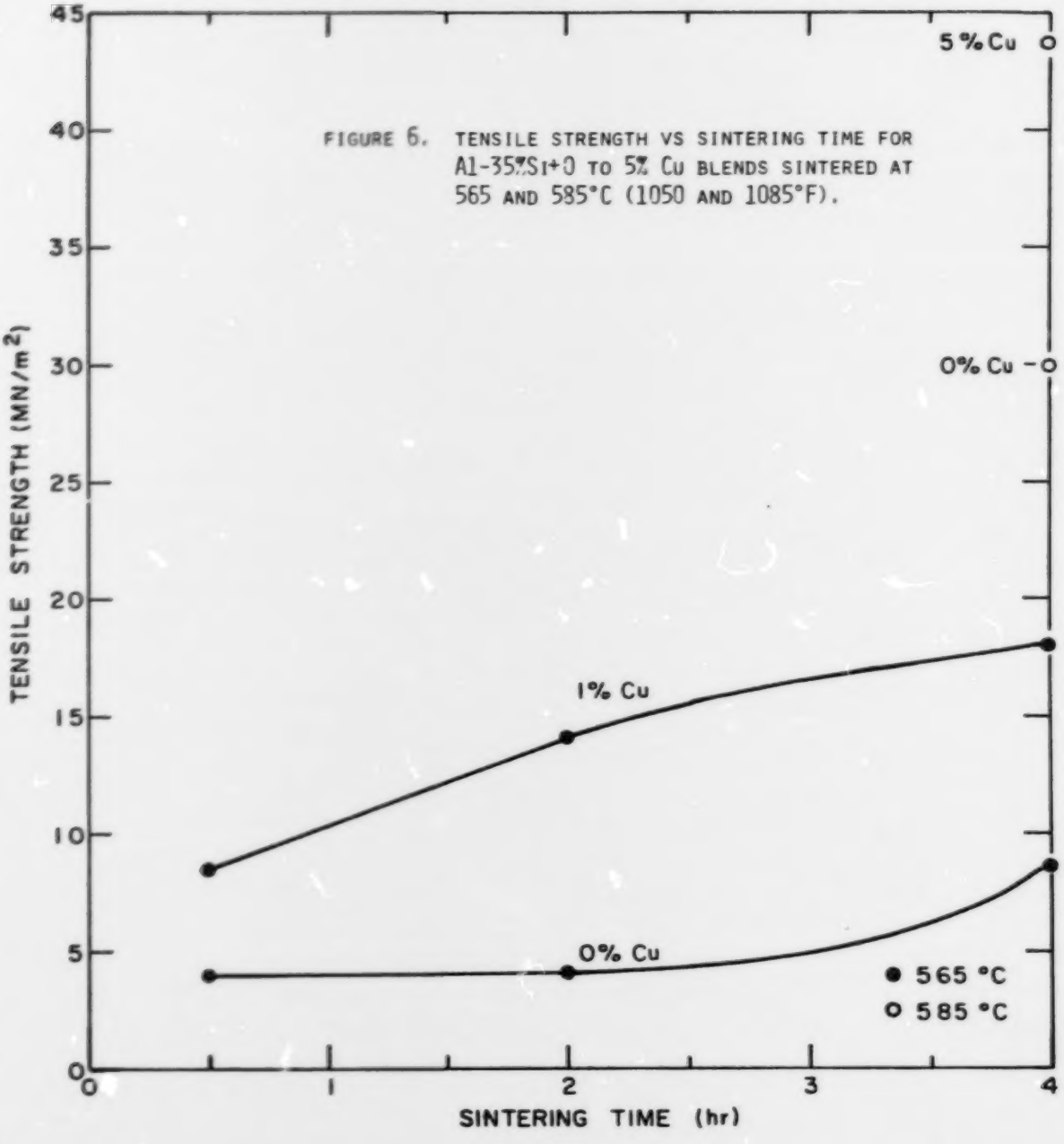


FIGURE 6. TENSILE STRENGTH VS SINTERING TIME FOR Al-35%Si+0 TO 5% Cu BLENDS SINTERED AT 565 AND 585°C (1050 AND 1085°F).

The tensile results listed in Table 3 and plotted in Figure 6 also show that the strength of Al-35% Si specimens sintered at 585°C (1085°F) for 4 hr is increased from 30 MN/m^2 to 43.9 MN/m^2 when blended with 5% copper powder. This effect of copper on the sinterability of specimens sintered at 585°C (1085°F) is not as apparent from the resistivity measurements because the values, 13.7 μ ohm-cm for the Al-35% Si specimen and 13.1 μ ohm-cm for the Al-35% Si + 5% Cu specimen, are in the range below 15 μ ohm-cm where resistivity is not as sensitive to the degree of sintering as the tensile strength. This, again, shows that the blended copper powder exerts little if any influence as a conductor in the sintered specimens.

The highest tensile strength for the sintered specimens tested is 45.3 MN/m^2 (Al-35% Si + 3% Cu sintered at 585°C, 1085°F for 6 hr) and this is much lower than for Al-35% Si hot-pressed material, 173 MN/m^2.

Some of the increase in tensile strength in the sintered specimens containing copper could be due to solution strengthening, but, at the strength levels obtained, the degree of sintering would be expected to be the most predominant factor.

Density

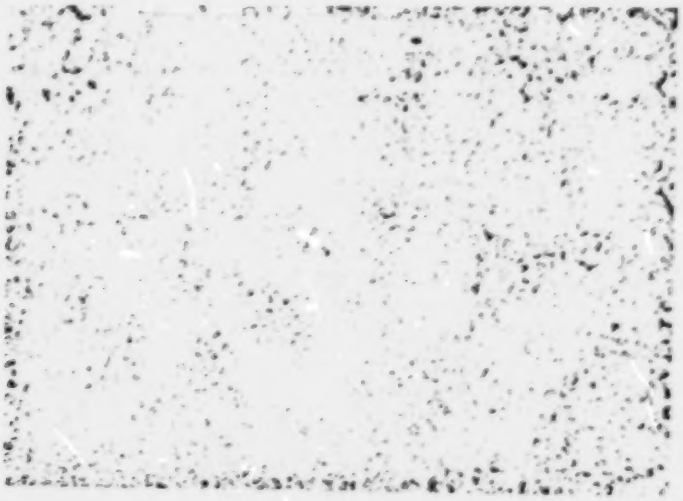
Densities of the sintered specimens are listed in Table 3 and plotted, along with the tensile strength, against resistivities in Figure 5. The densities follow the same pattern as the tensile strengths. Highest values for blends is 2.19 g/cc (Al-35% Si + 3% Cu sintered at 585°C (1085°F) for 6 hr) as compared to 2.50 g/cc for hot-pressed material.

Microexamination of Sintered Specimens

Microexamination of the sintered specimens was carried out to determine the effect of copper content and sintering time and temperature on the size of primary silicon particles. Sintering at 565°C (1050°F) does not affect the size of the primary silicon particles as can be seen by comparing a photomicrograph of the Al-35% Si powder, Figure 2, with that of a specimen sintered at 565°C (1050°F) for 4 hr, Figure 7. The presence of copper evidently increases the diffusion rate of silicon at this temperature because the primary silicon particles in Al-35% Si + 1% Cu and Al-35% Si + 3% Cu specimens sintered for 2 hr (Figures 8 and 9, respectively) are larger than in Al-35% Si specimens sintered for 4 hr (Figure 7). This increase in the size of primary silicon,

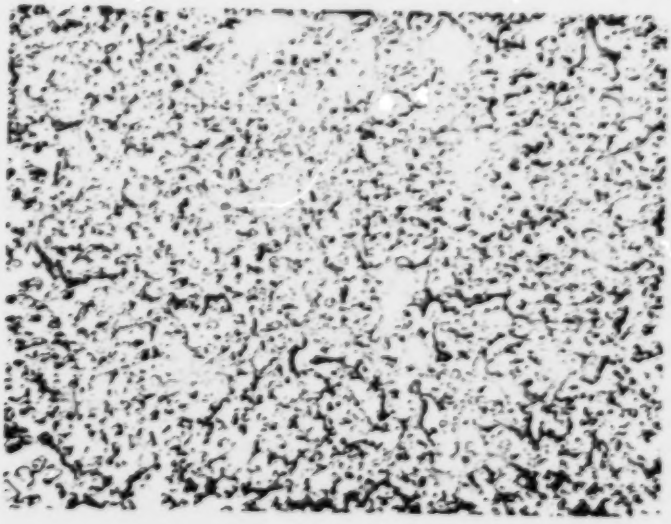
which occurs by some particles growing at the expense of others, should have little effect on tensile properties.

Increasing the sintering temperature to 585°C (1085°F) produces a substantial increase in the size of the primary silicon particles, and time at this temperature is also a factor, whereas copper additions have little effect. Figure 10 is a photomicrograph of an Al-35% Si specimen sintered at 585°C (1085°F) for 4 hr. Primary silicon particles of this size would have a detrimental effect on tensile properties and machinability.



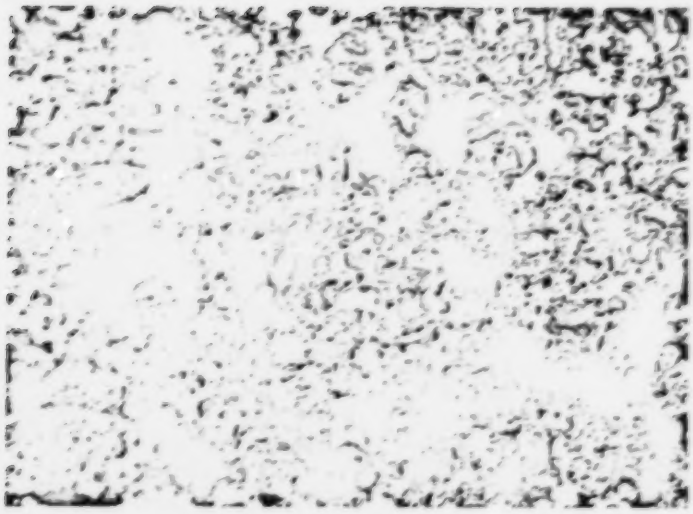
150X

Figure 7. Al-35% Si Sintered at 565°C (1050°F) for 4 hr.



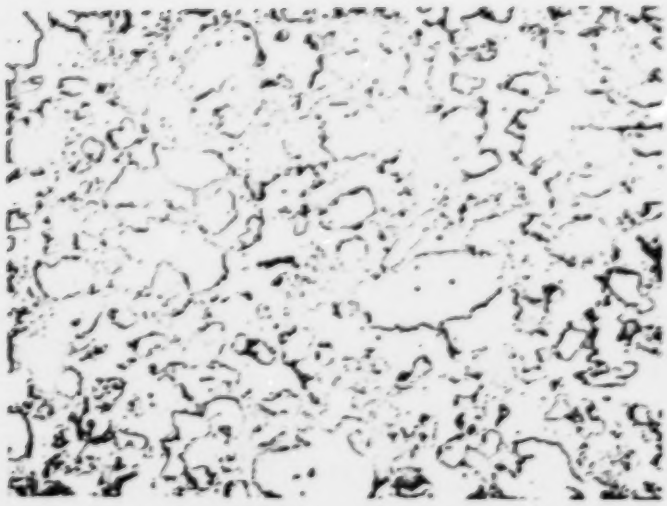
150X

Figure 8. Al-35% Si + 1% Cu Sintered at 565°C (1050°F) for 2 hr.



150X

Figure 9. Al-35% Si + 3% Cu sintered at 565°C (1080°F) for 2 hr.



150X

Figure 10. Al-35% Si sintered at 585°C (1085°F) for 4 hr.

CONCLUSIONS

1. Blending 1 to 5% copper powder with Al-35% Si pre-alloyed powder increases sinterability at 565 and 585°C (1050 and 1085° F). However, much more improvement is necessary to achieve tensile strengths comparable to that of hot-pressed material.

2. Mixing of an Al-40% Si + 12% Al + 5% Cu powder blend by grinding in an attritor does not improve sinterability over powders mixed in a Waring Blendor.

3. Sintering Al-35% Si specimens at 565°C (1050°F) does not affect the size of the primary silicon particles; but, in specimens containing copper there is some enlargement and increasing the sintering temperature to 585°C (1085°F) causes a marked growth of these particles in all specimens.

4. Electrical resistivity of Al-Si and Al-Si + Cu sintered specimens is related to the tensile strength and density. It is more sensitive than the other two properties for detecting trends during the early stages of sintering but is less sensitive as sintering progresses.

ACKNOWLEDGEMENTS

We wish to thank Mr. K. S. Milliken of the Metal Physics Section for designing a calculator program for computing electrical resistivity values.

REFERENCES

1. C. F. Dixon and H. M. Skelly; "Hypereutectic Aluminum-Silicon Alloys Produced by Powder Metallurgy Techniques". Int. J. of Powder Metallurgy, vol. 1, No. 4, pp 28-36 (1965).

2. H. M. Skelly and C. F. Dixon. "Aluminum-Silicon Powder Metallurgy Alloys". Int. J. of Powder Metallurgy, vol. 7, No. 3, pp 47-53 (1971).

3. G. D. Cremer and J. J. Cordiano. "Recent Developments in the Formation of Aluminum and Aluminum Alloys by Powder Metallurgy". Trans. Am. Inst. Mining and Met. Engrs., vol. 152, pp 152-162 (1943).

4. L. W. Kempf. "Properties of Compressed and Heated Aluminum Alloy Powder Mixtures", Powder Metallurgy, Edited by J. Wulff, American Society for Metals, Cleveland, Ohio, pp 314-316 (1942).

5. J. F. Kuzmick. "Some Experiments on the Effect of Pressure on Metal-Powder Compacts". Symposium on Production and Design Limitations and Possibilities for Powder Metallurgy Parts, Technical Publication No. 1788, Metals Technology, No. 12, pp 74-96 (January 1945).

6. R. L. Bickerdike. "Aluminum Components". Symposium on Powder Metallurgy. Iron and Steel Inst. Special Report No. 38, London, pp 185-191 (1947).

7. C. L. Goodzeit. "Method of Manufacturing Sintered Bearings". U. S. Patent 2,994,606, August 1961.

8. S. Storchheim. "Aluminum Powder Metallurgy Finally Made Commercially Practical". Progress in Powder Metallurgy, vol. 18, pp 124-130 (1962).

9. G. D. Lawrence and G. S. Foerster. "Aluminum-High Silicon Alloys". U. S. Patent 3,325,279, June 13, 1967.

10. J. H. Dudas and W. A. Dean. "The Production of Precision Aluminum P/M Parts". Int. J. of Powder Metallurgy, vol. 5, No. 2, pp 21-36 (1969).

11. R. Meyer. "The Measurement of Electrical Resistivity to Characterize a Sintered Product". Powder Metallurgy International, vol. 4, No. 2, pp 63-67 (1972).

12. J. R. Moon. "Powder Metallurgical Review 3, Sintering of Metal Powders. Powder Metallurgy International, vol. 3, No. 3, pp 147-152 (1971).

13. O. J. Zaverukha and P. S. Kislyi. "Investigation of the Sintering Process on the Basis of Changes in the Electrical Properties of Compacts on Heating". Soviet Powder Metallurgy and Metal Ceramics, No. 6(90), pp 469-471 (June 1970).

14. A. Duffield and P. Grootenhuis. "The Effect of Particle Size on the Sintering of Copper Powder". Journal of the Institute of Metals, vol. 87, pp 33-41 (1958-59).

15. J. Martinet and S. Tacvorian. "Electrical Conductivity of Powders During Sintering". Revue de Metallurgie, vol. 54, pp 54-70 (1957).

16. H. H. Hausner and J. H. Dedrick. "Electrical Properties as Indicators of the Degree of Sintering". The Physics of Powder Metallurgy, Edited by W. E. Kingston, McGraw Hill, New York, 1951, pp 320-343.

17. H. H. Gegenwarth. "Correction Factors for a Two-Point Probe Resistivity Measurement of Cylindrical Crystals". J. of Electrochemical Soc, vol. 116, No. 8, pp 1166-1167 (August 1969).

18. A. S. M. Metals Handbook, 8 ed., 1961, vol. 1, Properties and Selection of Metals, p 48.